Design and Scalable Assembly of High Density Low Tortuosity Electrodes

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Presenter:

Massachusetts Institute of Technology, Cambridge, MA

Date: 06-10-2015

Project ID: ES071

Overview

Timeline

- Project start: May 22, 2013
- Project end: April 3, 2017
- 50% complete

Budget

- Total project funding
  - DOE share: $1,075,344
  - Contractor share: $0
- Funding received in FY13
  - $256,983
- Funding for FY14
  - $265,637
- Funding for FY15
  - $270,000

Barriers

- Lowering cost and increasing energy density of Li-ion batteries by reducing inactive content
- Achieve 3x times the area capacity (mAh/cm^2) of current technology under EV duty cycles
- Achieving sufficient electronic conductivity in additive-free dense thick electrodes.

Partners

Collaborations: Antoni P. Tomsia, LBNL

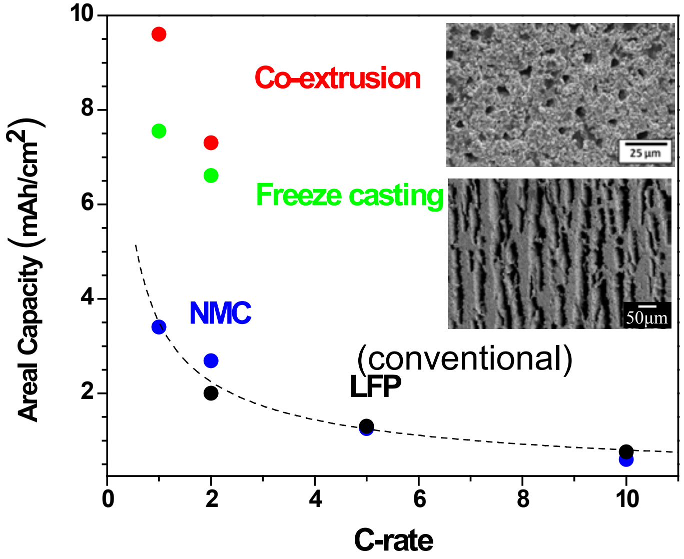
- Sample fabrication

Project lead: MIT

Relevance

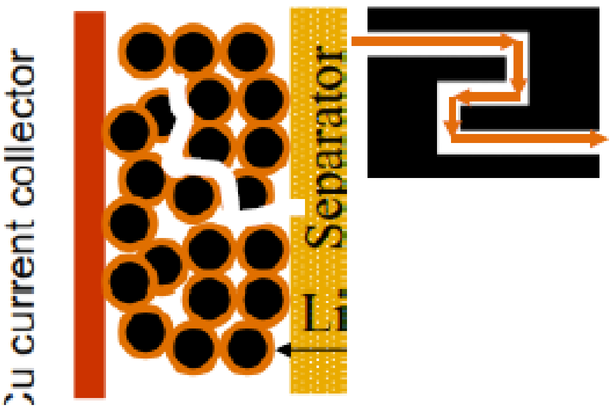
- The high inactive materials content of current Li-ion batteries contributes directly to high battery cost, and reduces specific energy and energy density.
- The number of separator and current collector layers per Ah of cell capacity is inversely proportional to the area capacity (mAh/cm^2) of the electrode.
- Area capacity can be increased arbitrarily by increasing electrode thickness and/or density, but does not contribute *usable* energy unless the capacity can be accessed at practical C-rates.
- Thus, concepts that can provide higher usable area capacity, e.g. during ~2C pulses in a EV or PHEV drive cycle, are needed.
- Electrodes having high active materials density and low tortuosity porosity can provide such benefits, but scalable processes are needed.

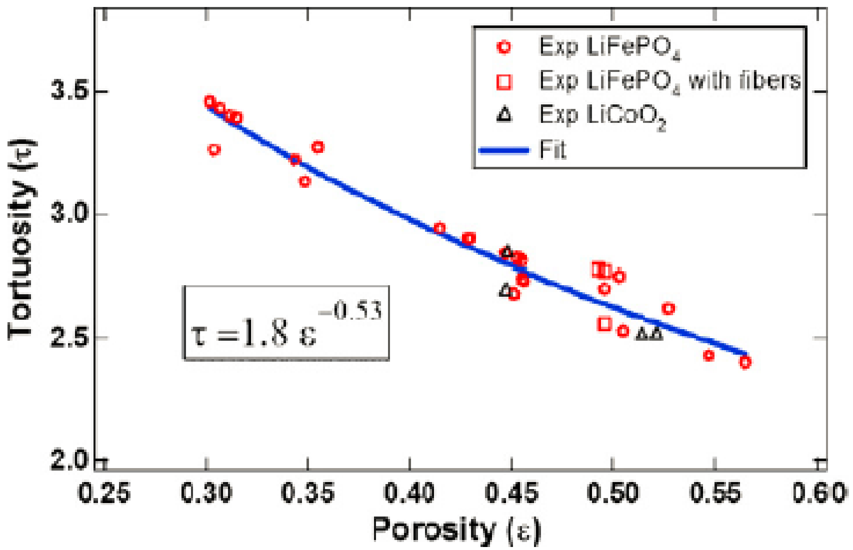
(Bae et al. *Adv.Mater*. 2013, *25*, 1254–1258, and present work.)



Relevance

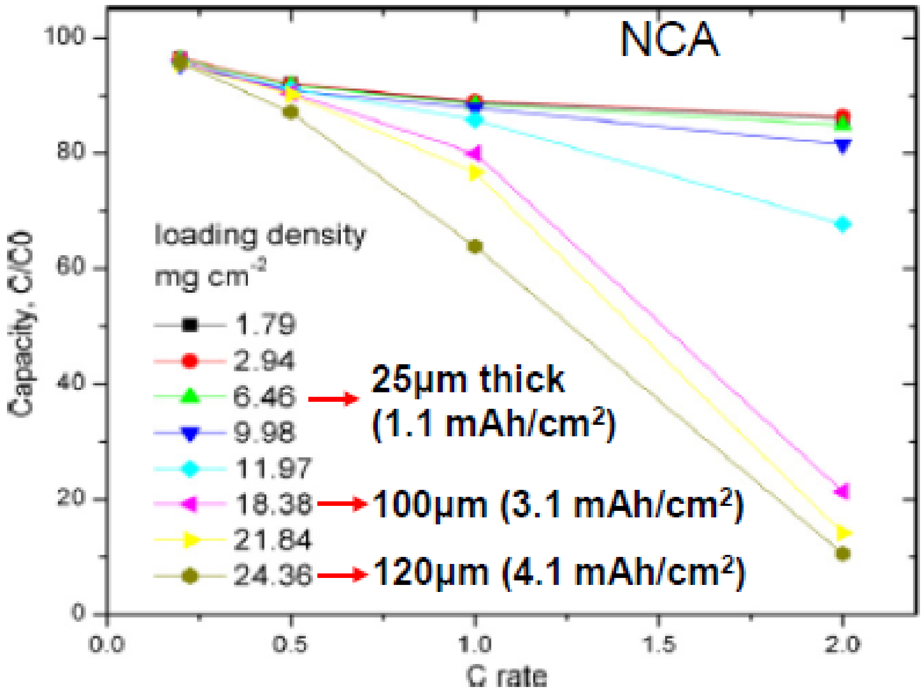
Conventional composite electrode





I.V. Thorat, et al., J. Power Sources 188, 592-600 (2009)

Discharge capacity for various electrode loadings in typical composite NCA electrode



Wenquan Lu et al., J. Power Sources, 196 (2011) 1537

Objectives

Overall Objective: Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density over conventional Li-ion technology.

Objectives in detail (March 2014 – March 2015):

- Down-select cathode compounds based on electronic and ionic conductivity.
- Fabricate and test additive-free, dense oxide cathodes having oriented low-tortuosity pore structure using directional freeze-casting + sintering
- Fabricate powder-based graphite anodes having oriented low-tortuosity pore structure using directional freeze-casting without sintering
- Develop magnetic orientation method for fabricating electrodes with oriented low-tortuosity pore structure
- Quantify the tortuosity of the fabricated electrodes.
- Electrochemical testing of electrodes targeting area capacity of at least 5mAh/cm^2 under 1C continuous rate and 10mAh/cm^2 under 2C, 30 sec pulse.
- Electrochemical testing of anode electrodes targeting area capacity of at least 5mAh/cm^2 under 1C continuous rate and 10mAh/cm^2 under 2C, 30 sec pulse.

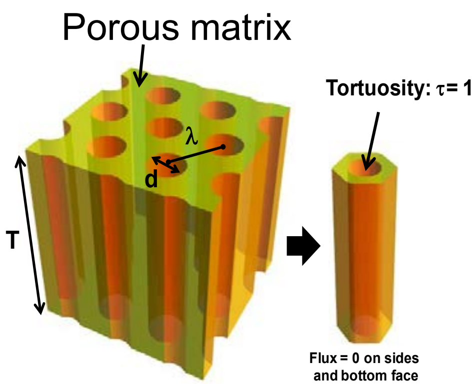
Milestones

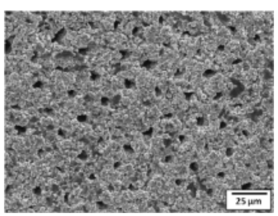
Quarter	Milestones/Deliverables Description and Due Date
Q1 10/1/14- 12/31/14	Fabricate and test at least one anode compound in an electrode structure having at least 10 mAh/cm^2 theoretical capacity. (12/31/14) Completed
Q2 1/1/15- 3/31/15	Demonstrate at least 5 mAh/cm^2 capacity per unit area at 1C continuous cycling rate for at least one candidate anode. (3/31/15) Completed
Q3 4/1/15- 6/30/15	Go/No-Go (revised) *Demonstrate an electrode with at least 7.5 mAh/cm^2 that passes the USABC dynamic stress test (DST) with peak discharge C-rate of 2C*. (6/30/15)
Q4 7/1/15- 9/30/15	Demonstrate an anode with at least 10 mAh/cm^2 capacity per unit area for a 2C 30 sec pulse. (9/30/15)

Approach

Earlier Proof of Concept

- Dual scale porosity - channels and matrix
- Co-extrusion/sintering process





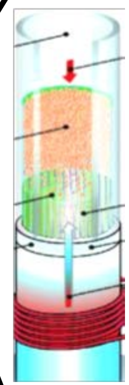
Bae, et al., Adv. Mater., **25** (2013) 1254

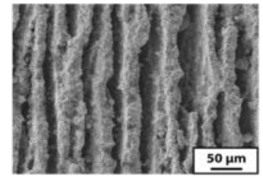
Materials in program: LCO, NMC, LMNO, NCA, graphite

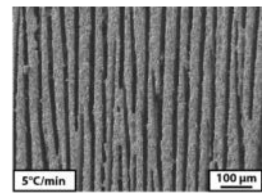
Current Work

(1) Directional Freezing

(a) Sintered



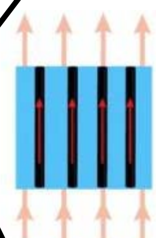


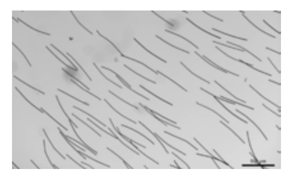


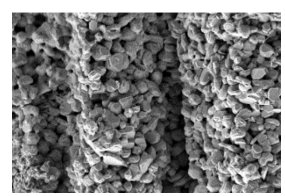
(b) Non-sintered

(2) Magnetic Alignment

(a) Sacrificial solids

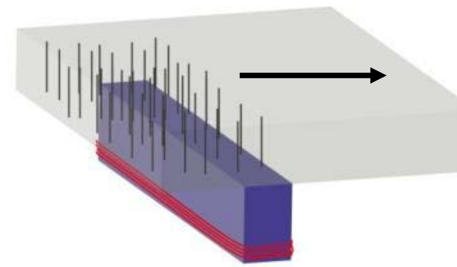




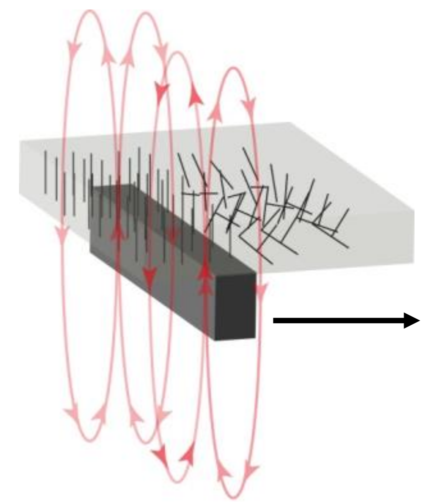


(b) Emulsion chaining

Future Development of Scalable Processes



Planar geometry with normal orientation



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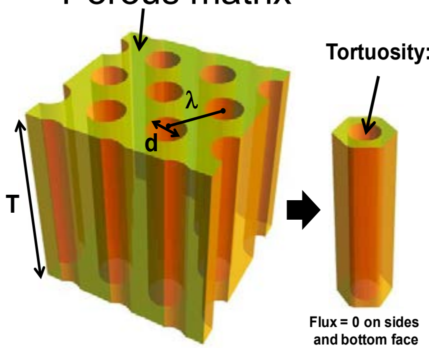

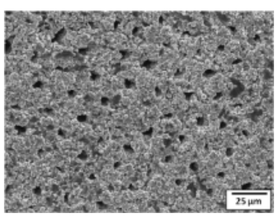

Bae, et al., Adv. Mater., **25** (2013) 1254

New for 2014-2015

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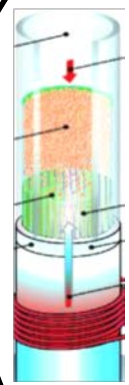

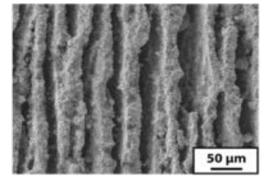

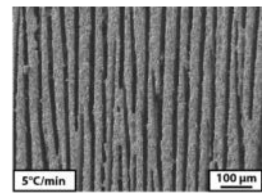

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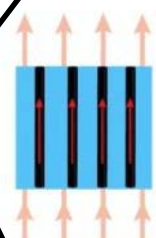

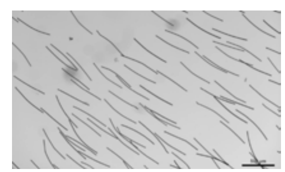

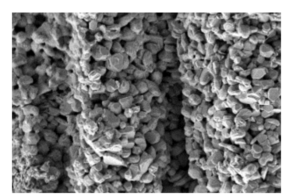

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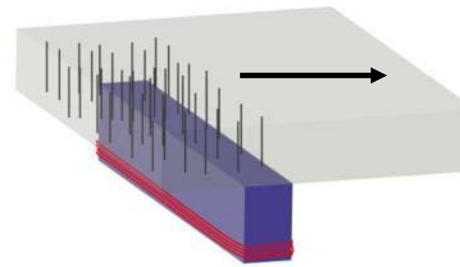

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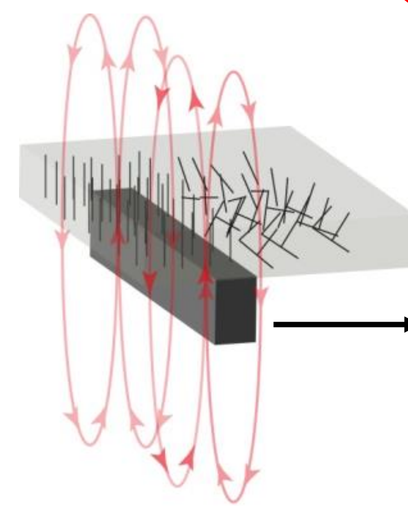
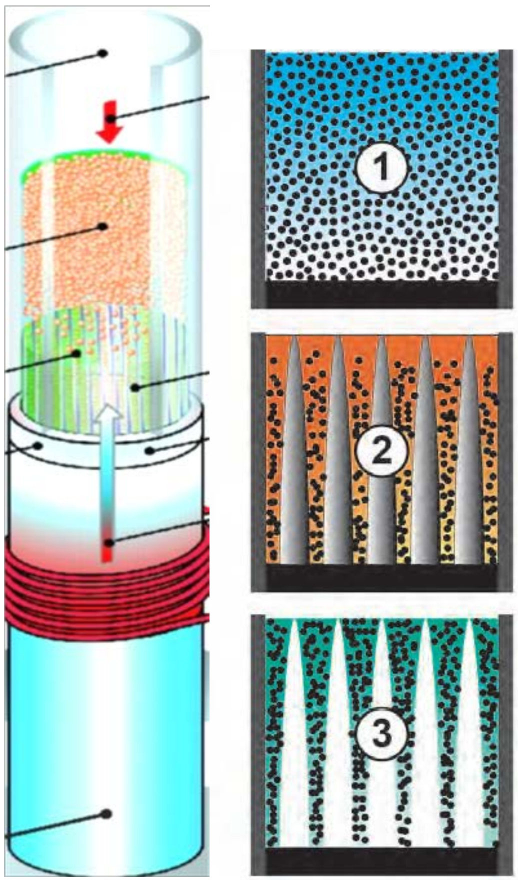


Approach

Freeze-Casted Electrode Fabrication:

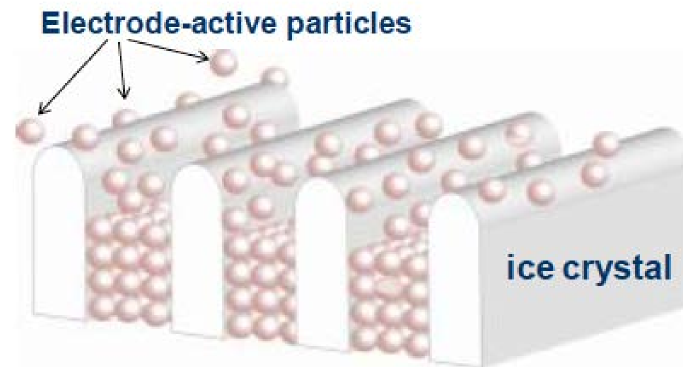


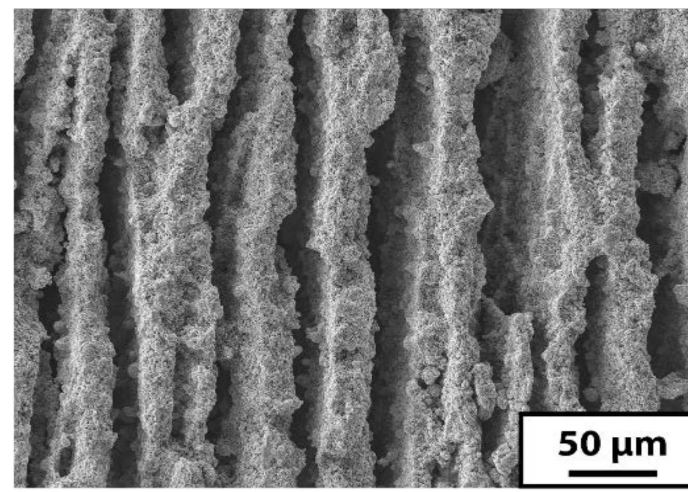
NCA slurry is poured into mold at room temperature

As ice lamellae grow, they force suspended particles into voids

Frozen structure is lyophilized, sublimating ice and generating porosity

Schematic of freeze casting process

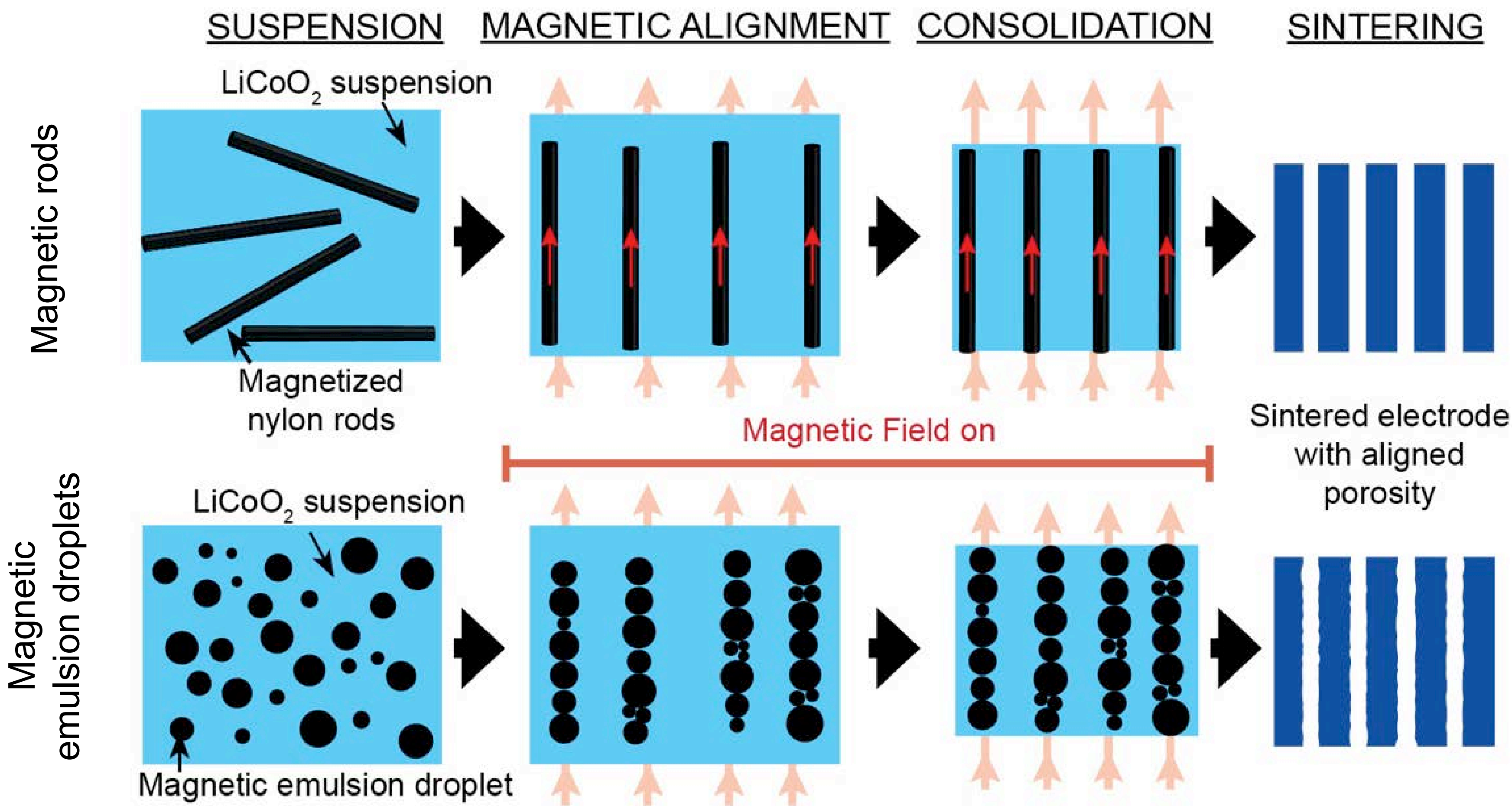




Microstructure depends on:
- ❖ **Rate of solidification**
- ❖ **Solid content in the slurry**
- ❖ **Sintering temperature**

Approach

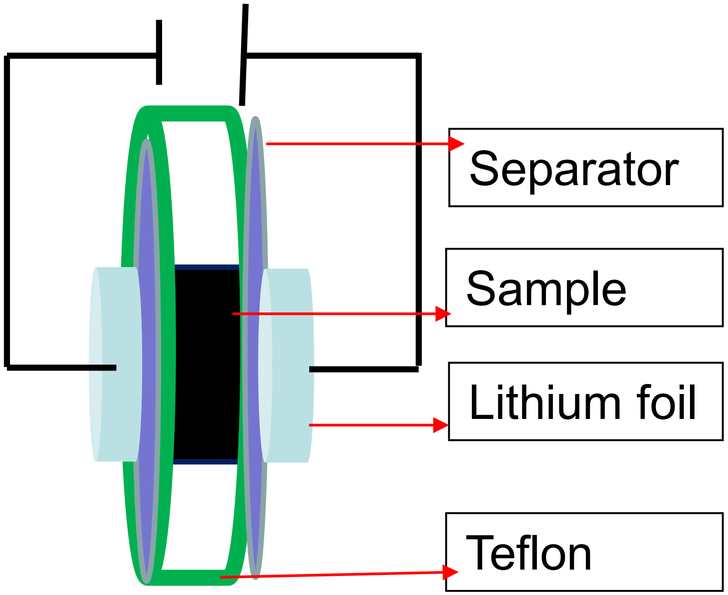
Magnetic alignment:



Electrode particle slurry is mixed with a sacrificial magnetic phase (nano iron oxide)	Magnetic phase is aligned in a magnetic field	Solvent removal	The sacrifical phase is removed by combustion or evaporation

Approach

Tortuosity measurement:

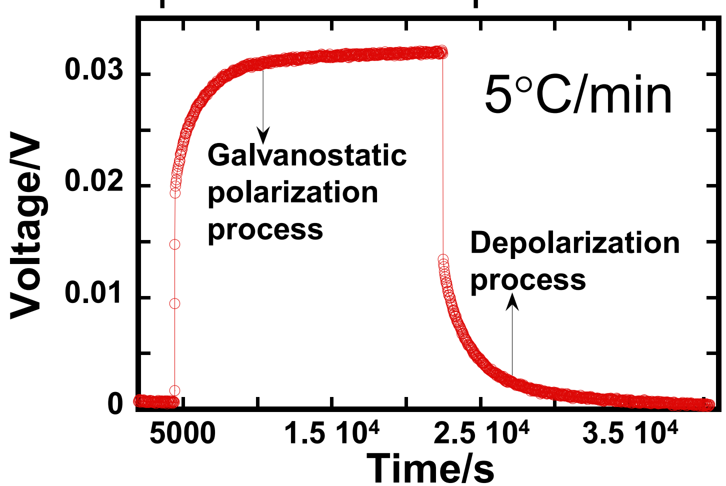


Electrochemical cell was employed to determine the tortuosity of directional fabricated electrodes by ac and dc techniques.

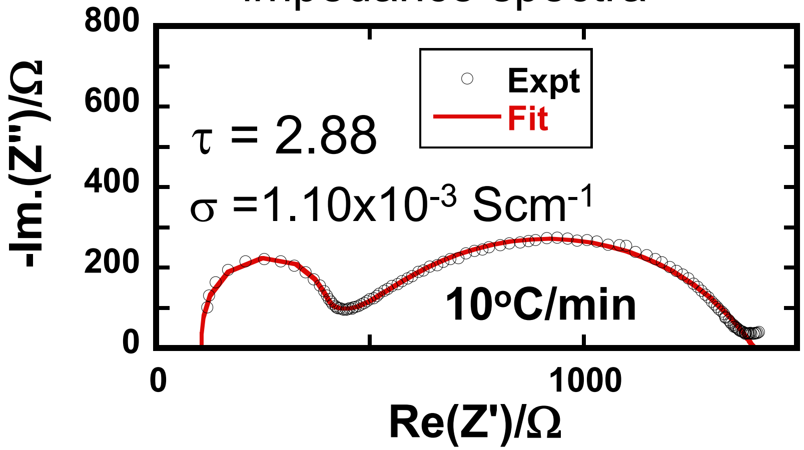
$$U_{ion} = \frac{i_p L}{\sigma_{tot}} + \frac{\sigma_{eon}}{\sigma_{tot}} \frac{i_p L}{\sigma_{ion}} \left\{ 1 - \frac{8}{\pi^2} \exp\left[-\frac{t}{\tau^{\delta}} \right] \right\}$$

$\ln(U - U_{\infty})$ vs. t

Dc polarization-depolarization



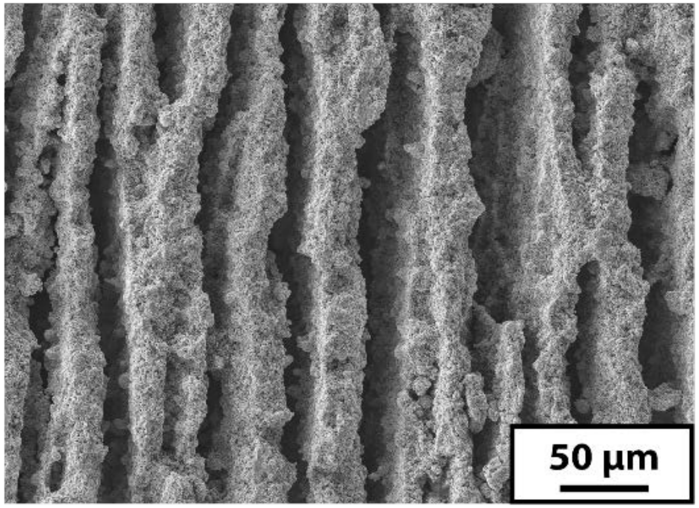
impedance spectra



Technical Accomplishments

Freeze-cast and sintered NCA microstructures at different freezing rates

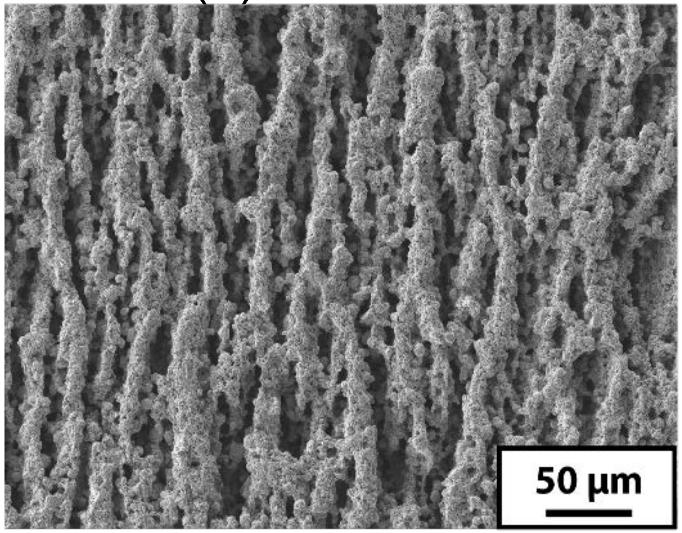
(a) 5°C/min



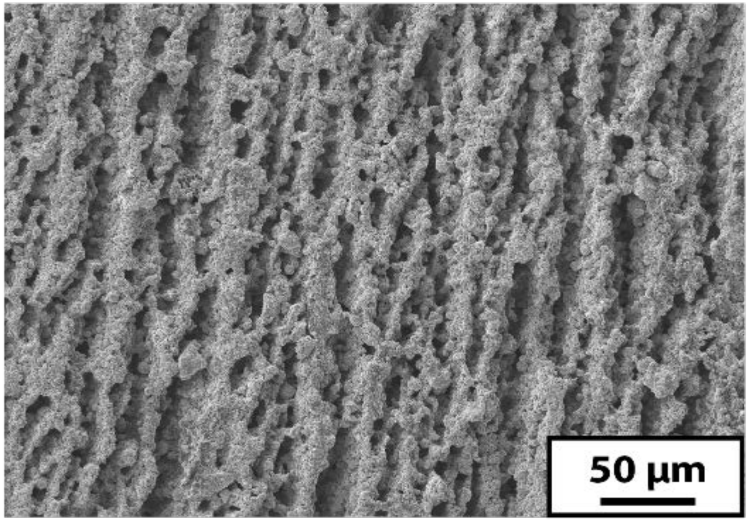
Higher cooling rates:

- Decreased lamellae thickness
- Increased channel diameter
- Pore channels are not as well defined as slow cooling

(b) 7.5°C/min

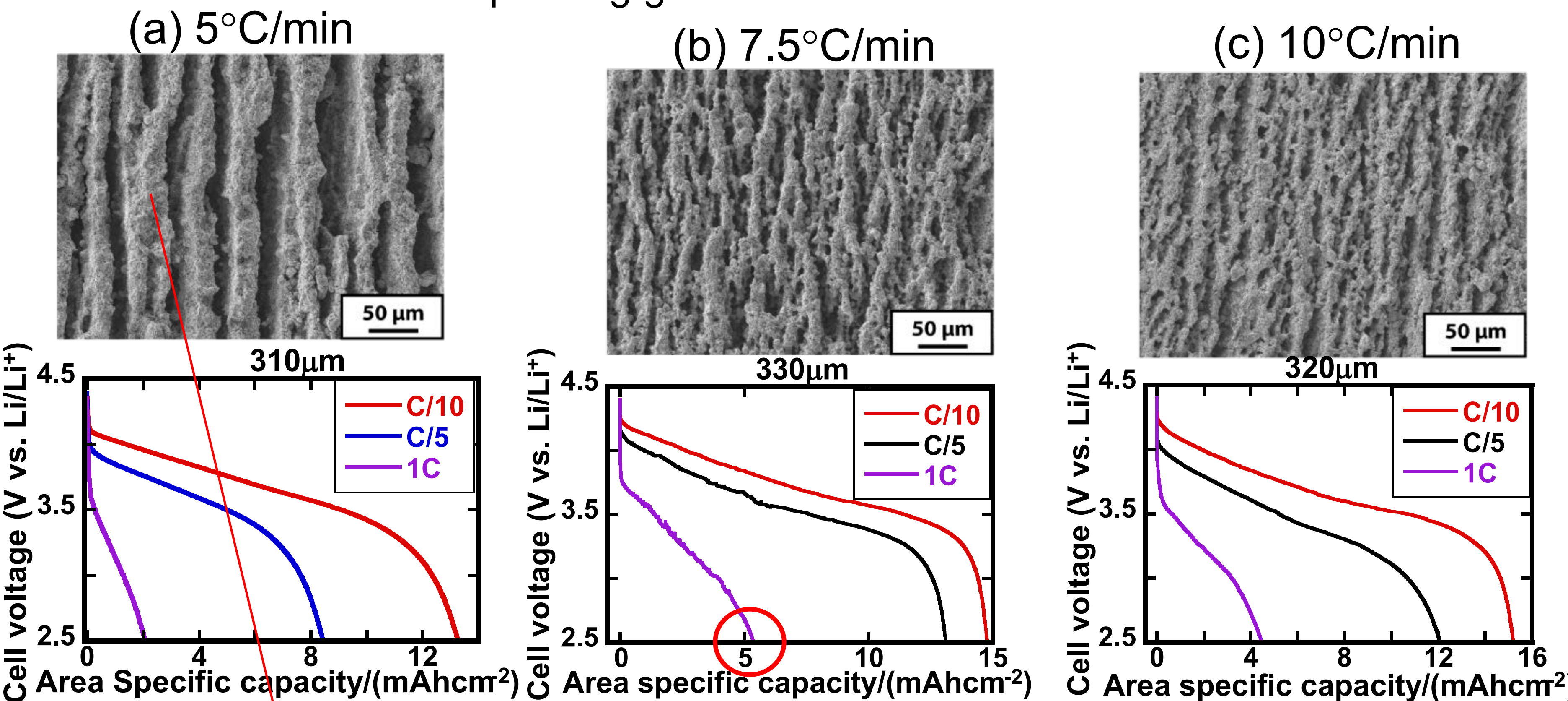


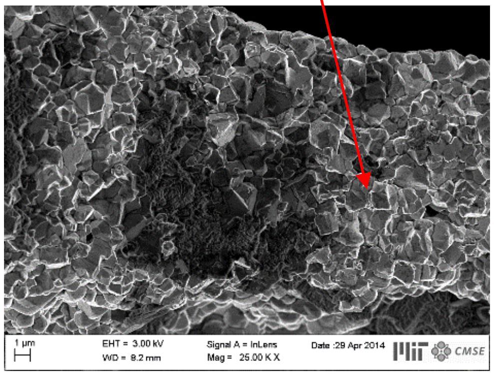
(c) 10°C/min

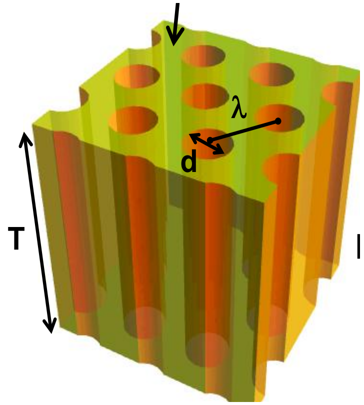


Technical Accomplishments

Corresponding galvanostatic test results on NCA



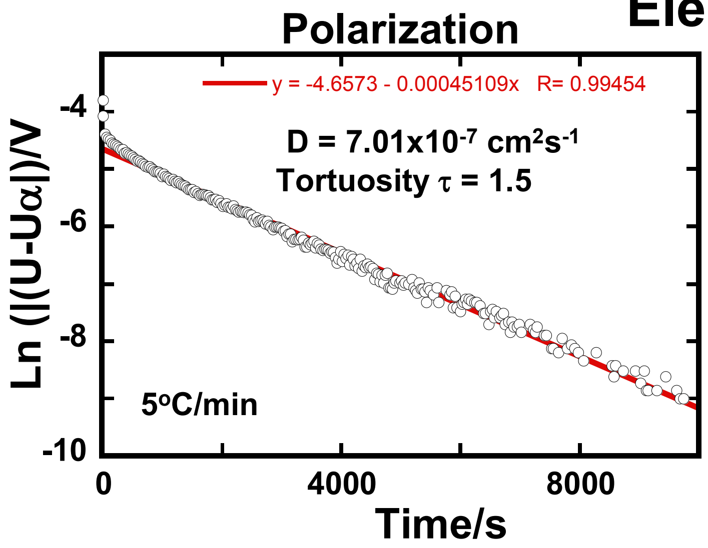


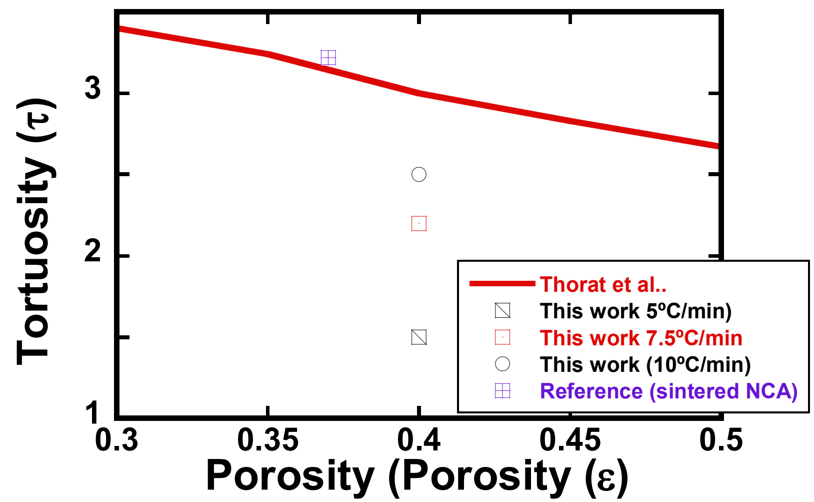


Dual-scale porosity (linear pores and porous matrix) determines effective tortuosity. Sample (b) showing 5 mAh/cm^2 at 1C rate met Q2 milestone.

Technical Accomplishments

Electrode tortuosity





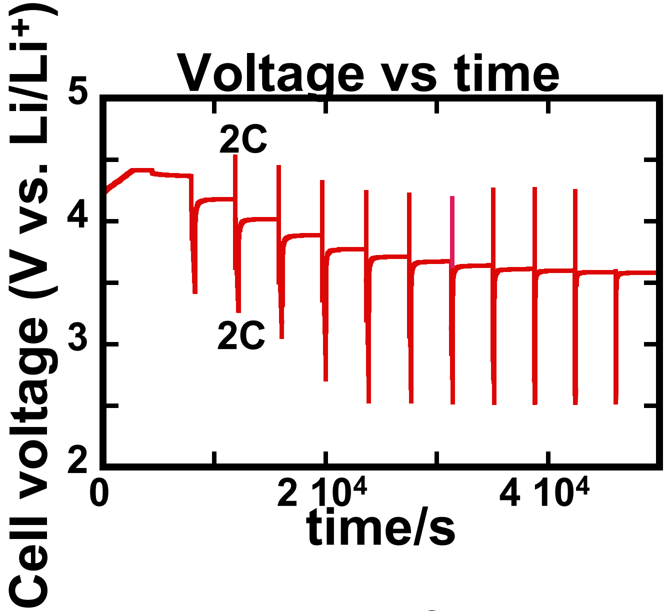
Sample	Tortuosity (τ) (dc method)
5°C/min	1.5
7.5°C/min	2.2
10°C/min	2.5
7.5°C/min	2.6
10°C/min	2.8

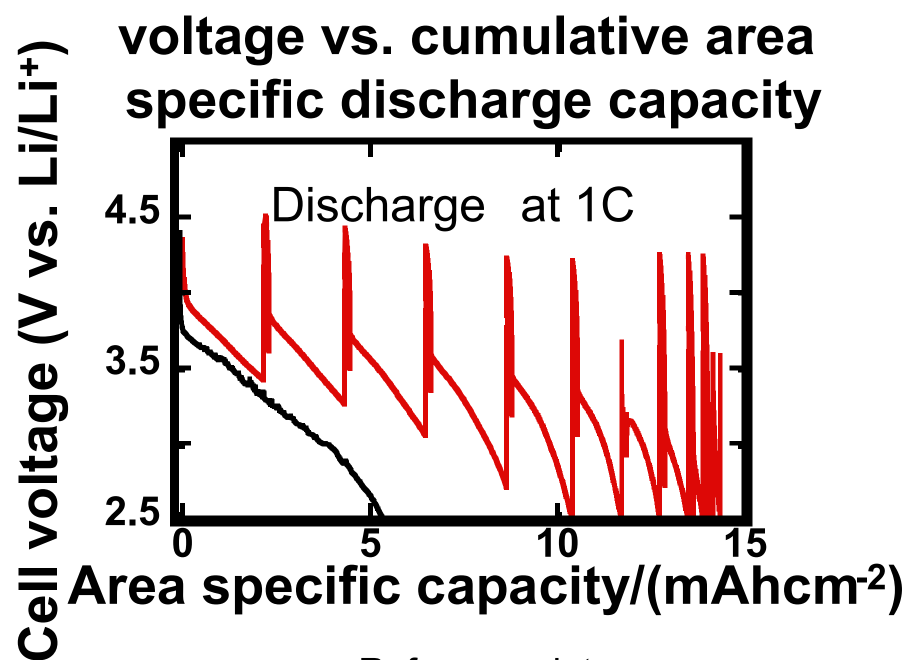
- ❖ Slowest freezing (5°C/min) produces lowest tortuosity
- ❖ All directional freeze-cast samples have lower tortuosity than reported for composite electrodes.
- ❖ Tortuosity obtained from ac and dc measurements agree well

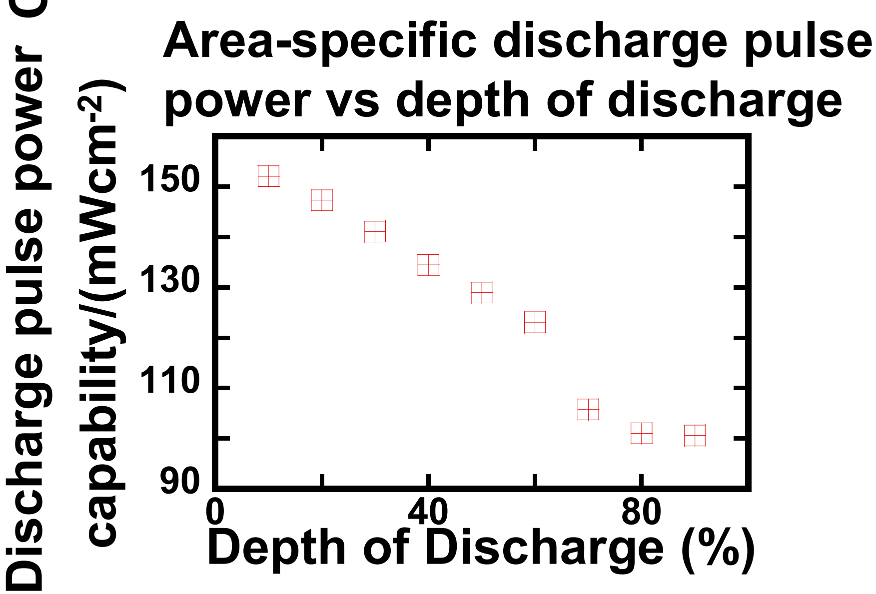
After Thorat et al., Journal of Power Sources 188 (2009) 592

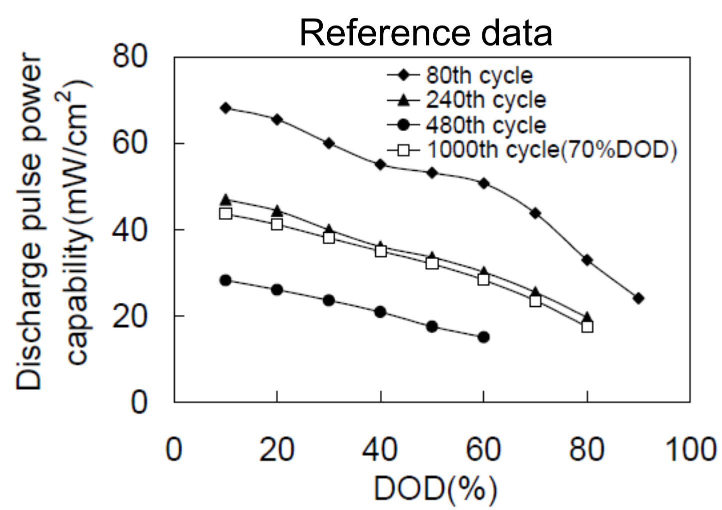
Technical Accomplishments

Hybrid pulse power characterization (HPPC) for NCA (b) at 300μm thickness





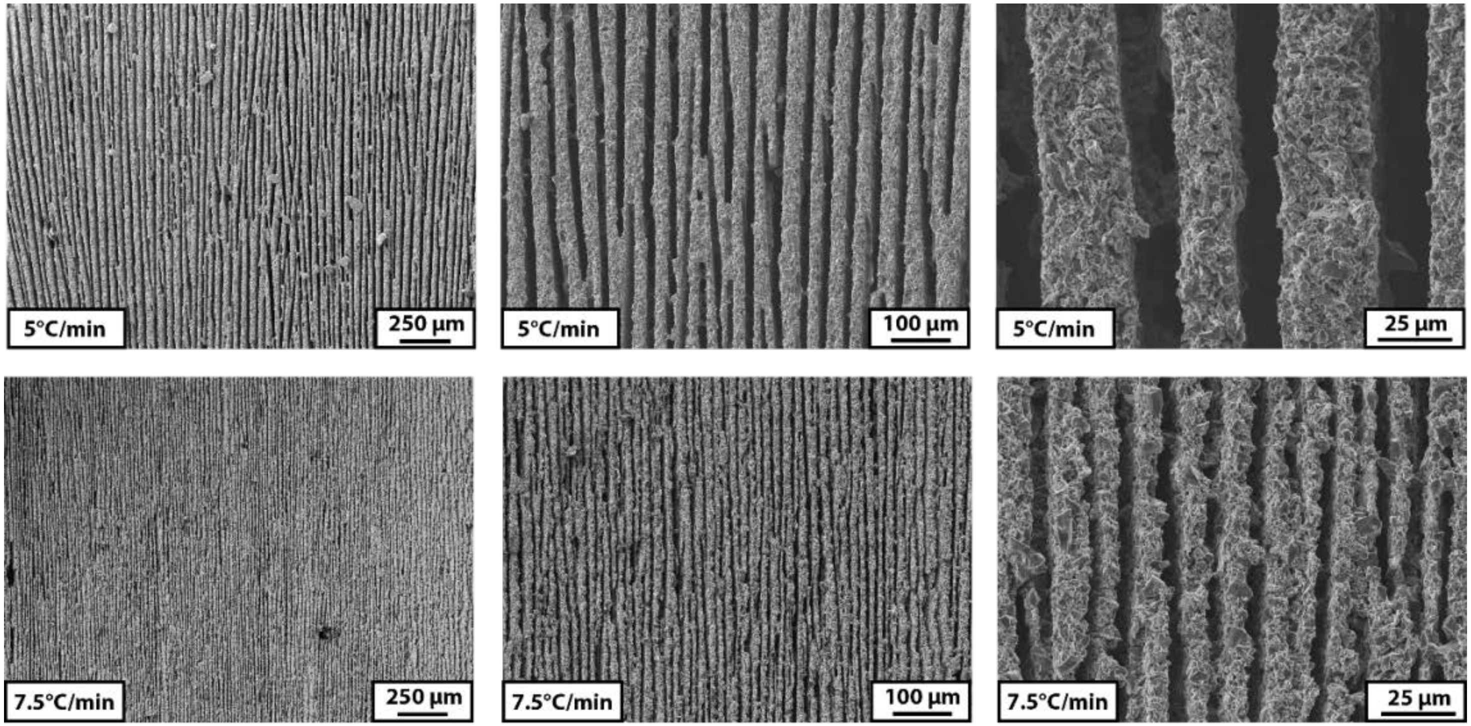




J. Shim et al., Journal of Power Sources 122 (2003) 188

Technical Accomplishments

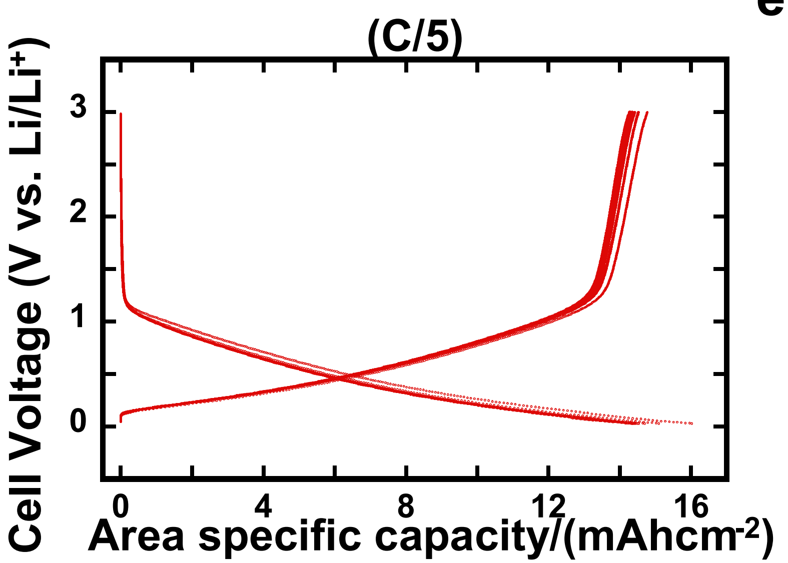
SEM micrographs of *unsintered* graphite particulate anode made by directional freezing

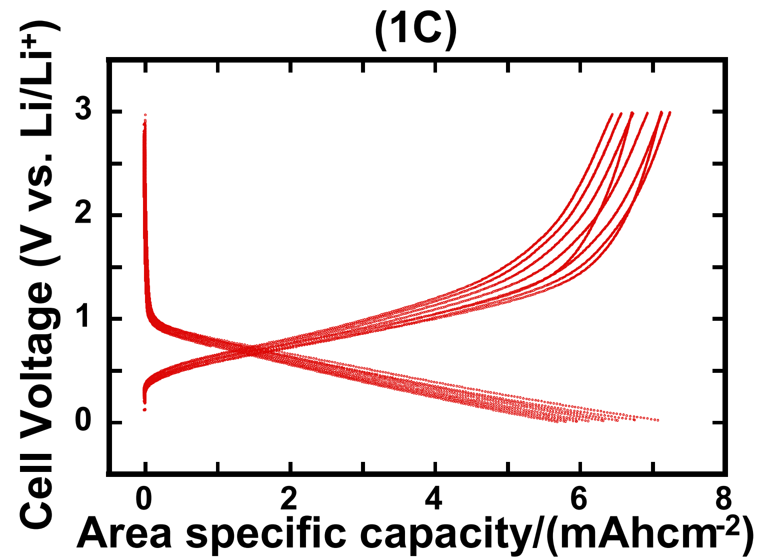


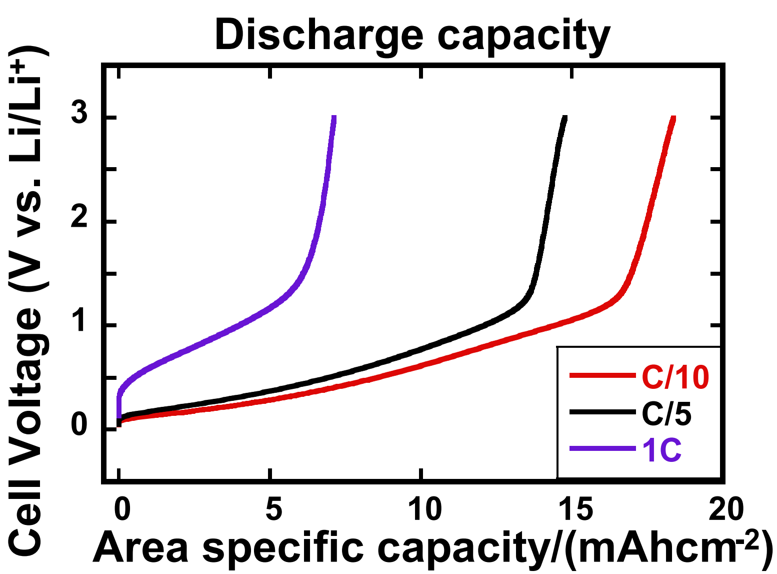
- Water-based electrode formulation: 5% CMC
- 30 vol% graphite content in starting suspension
- Vacuum dried without sintering
- 58-60 vol% porosity in current samples
- 800µm thick electrode has ~25mAh/cm^2 theoretical capacity

Technical Accomplishments

Testing: 800 μm thick unsintered freeze-cast (7.5°C/min) graphite electrode



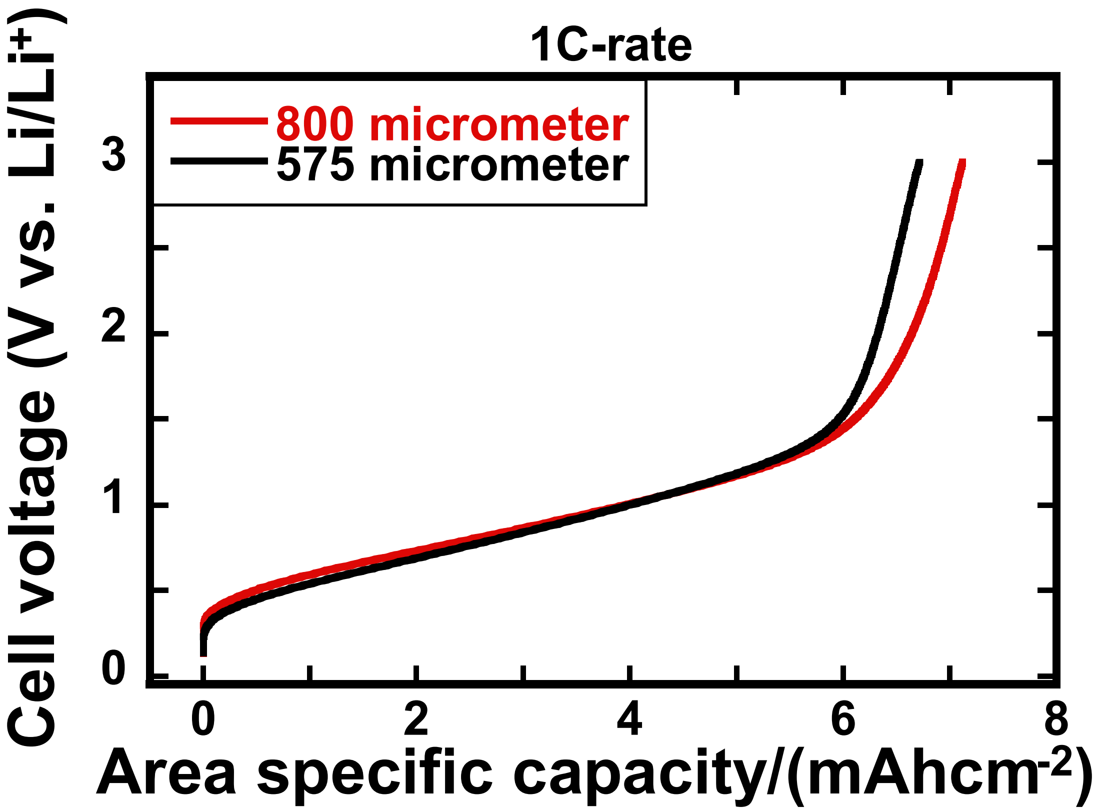




- Rate capability is probably electrolyte transport limited at 800 μm thickness
- Tortuosity to be characterized
- Met Q2 milestone (>5 mAh/cm^2 at 1C rate continuous cycling)
- Dynamic Stress Tests to follow

Technical Accomplishments

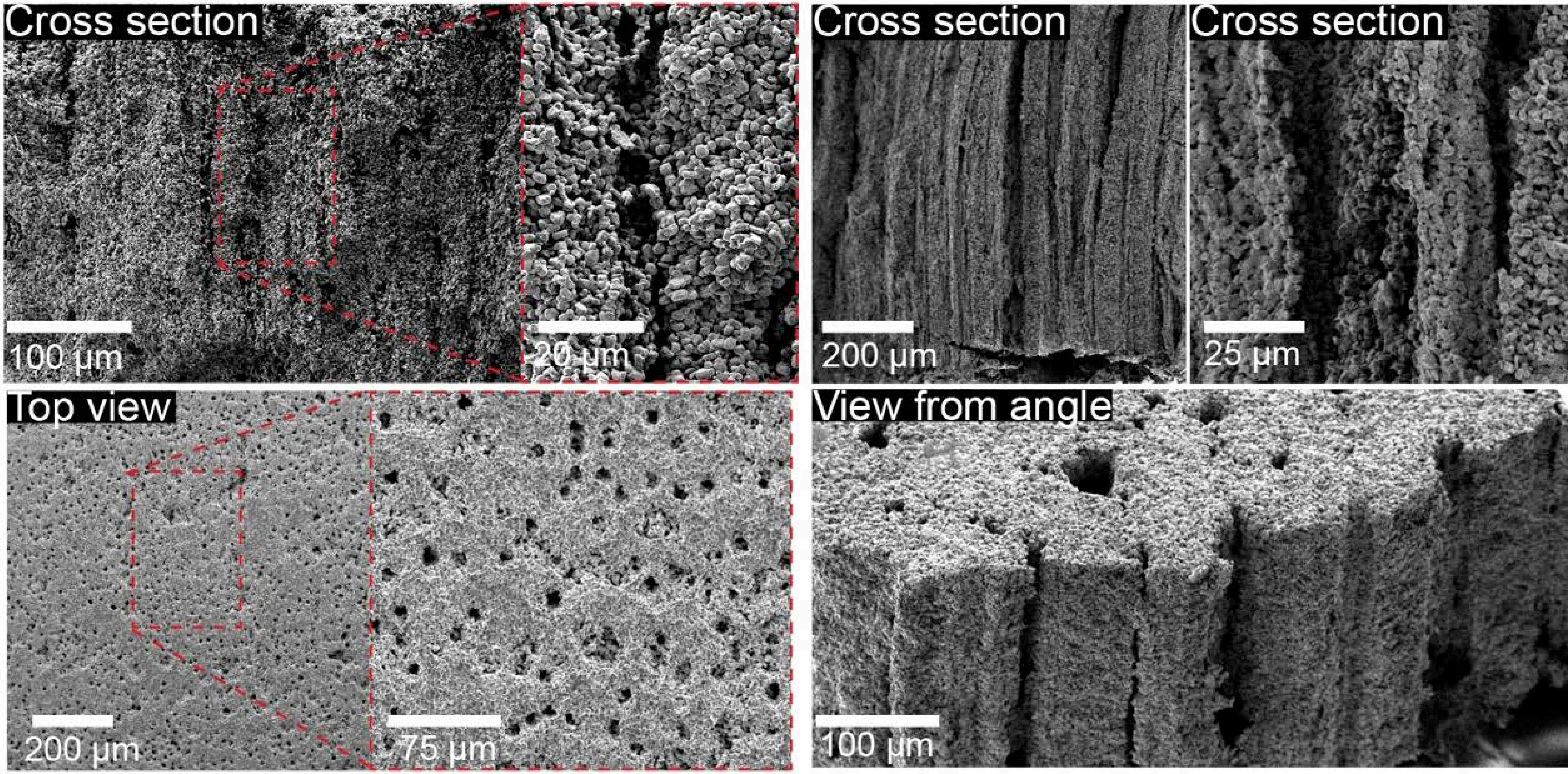
Q2 2015 Milestone: Demonstrate at least 5 mAh/cm^2 at 1C rate continuous cycling rate for at least one anode



Technical Accomplishments

$LiCoO_2$ electrode fabrication using magnetic alignment of sacrificial pore former

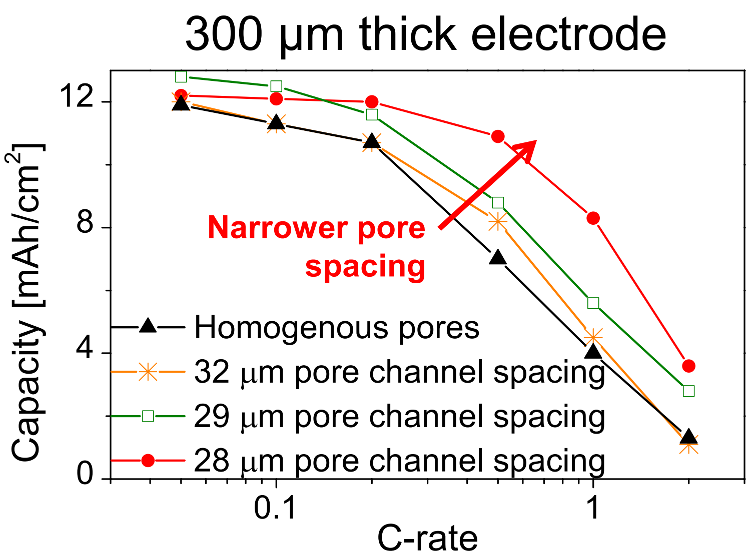
Aligned sacrificial polymer rods | Chaining of emulsion droplets

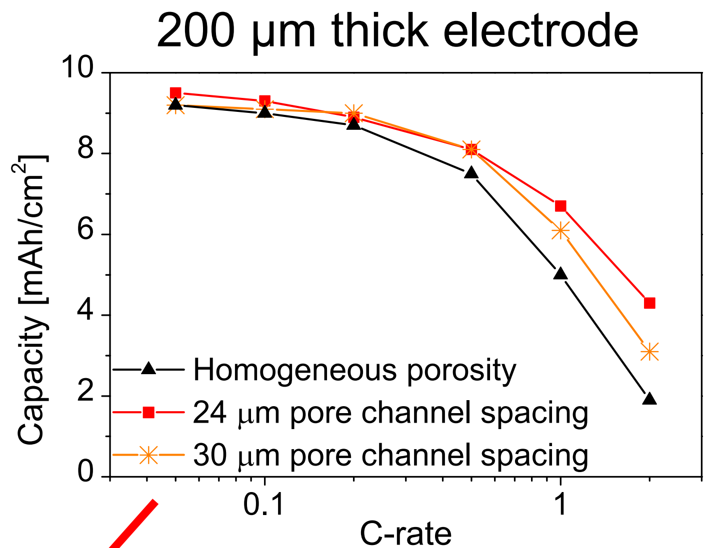


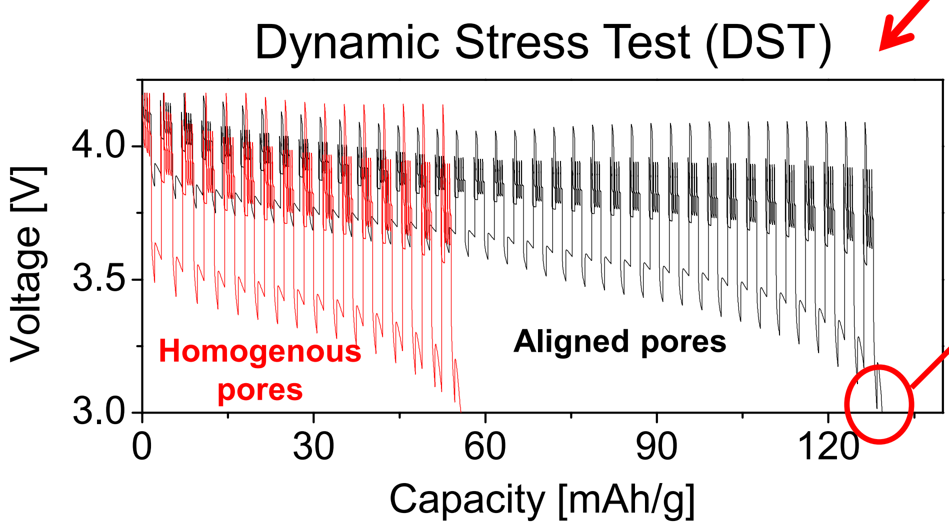
Cathodes with aligned pore channels successfully produced by both methods.

Technical Accomplishments

Electrochemical testing: From standard galvanostatic tests towards EV drive cycles (e.g., Dynamic Stress Test (DST))







200 μm thick electrodes with aligned porosity deliver 8.1 mAh/cm^2, 125 mAh/g $LiCoO_2$ capacity in DST protocol.

Response to previous year Reviewers' Comments

Is the directional freezing process too expensive for DOE goals, and can it be modified to reduce need for sintering?

- Directional freezing without sintering has been demonstrated for graphite suspensions this year. In addition an alternative magnetic alignment approach expected to be of lower cost has been demonstrated.

What about performance at higher rates? (From multiple reviewers)

- This year's tests emphasize drive-cycle testing with realistic battery scaling factors. Electrodes from both directional-freezing and magnetic alignment approaches have shown promising results under HPPC and/or DST duty cycles.
- Modeling and experiment to understand how pulse response correlates with continuous discharge response is underway.

Response to previous year Reviewers' Comments

Is approach limited to highly electronically conductive materials, and if so what are the implications? Can conductive additives be incorporated to get around electronic conductivity limitations?

- Sintered NCA electrodes were shown to have sufficient electronic conductivity to perform in HPPC tests
- Directional-freezing has been successfully applied to aqueous formulation graphite anodes that include conductive additives. Magnetic alignment is being evaluated for similar suspensions.

Additional national lab or industry collaborations are recommended

- The move to drive-cycle testing is being done with advice from industry as to which tests are most valued. Future plans include scaling to a cell size of interest to industry validators.

Collaboration/Coordination with Other Institutions

- Collaboration with A.P. Tomsia group at Lawrence Berkley National Laboratory (LBNL) for fabrication of directionally freeze-cast electrodes
- Collaboration (no funds exchanged) with Prof. Randall Erb at Northeastern University on magnetic alignment
- Dr. Jonathan Sander (magnetic alignment project) is supported by a Swiss government fellowship

Remaining Challenges and Barriers

- Magnetic alignment approach demonstrates for the first time a facile process for producing aligned porosity normal to the plane of a thin electrode. In the next phase, the following should be addressed:
  - What is uniformity across the plane and through the thickness?
  - Can the approach be applied to a non-sintered electrode, and adapted to current electrode processing paradigms?
  - Are the small amounts of magnetic phases introduced into the electrodes truly benign?
- The freeze-casting approach needs to be adapted to higher speed, thin-electrode configuration as well.
- There is mounting evidence that the dynamic response of thick low-tortuosity electrodes such as those developed in this program differs significantly from conventional thin electrodes. Specifically, the drive-cycle performance cannot be easily predicted from standard galvanostatic tests over a range of C-rates. A detailed transport model for such electrodes needs to be developed.

Proposed Future Work

Rest of FY 2015

- Tailor the microstructure with dual porosity in unsintered graphite electrode in pursuit of the Milestones and Objectives of the project.
- Change testing approach to emphasize drive-cycle type tests that provide more realistic evaluation of electrode performance in EV applications.
- Change milestones accordingly to focus on results from DST tests.

FY 2016

- Expand work on magnetic alignment given recent successes
- Develop directional freeze-casting methodology for planar electrode geometry.
- Develop model to understand and predict electrode response under drive cycle testing
- Construct and test full Li-ion cells

Presentation Summary

- Electrode structures with aligned pore channels have been successfully produced in cathode and anode materials by directional-freeze casting and magnetic alignment techniques. The magnetic alignment approach is newly developed for 2014-2015.

- Microstructure of freeze-cast samples can be systematically varied (i.e. channel diameter and spacing, porosity of matrix) by controlling freeze-casting rate and sintering conditions. The oriented pore microstructure reduces measured electrode tortuosity to as low as τ = 1.5. Both oxide cathodes and graphite anodes have been demonstrated.

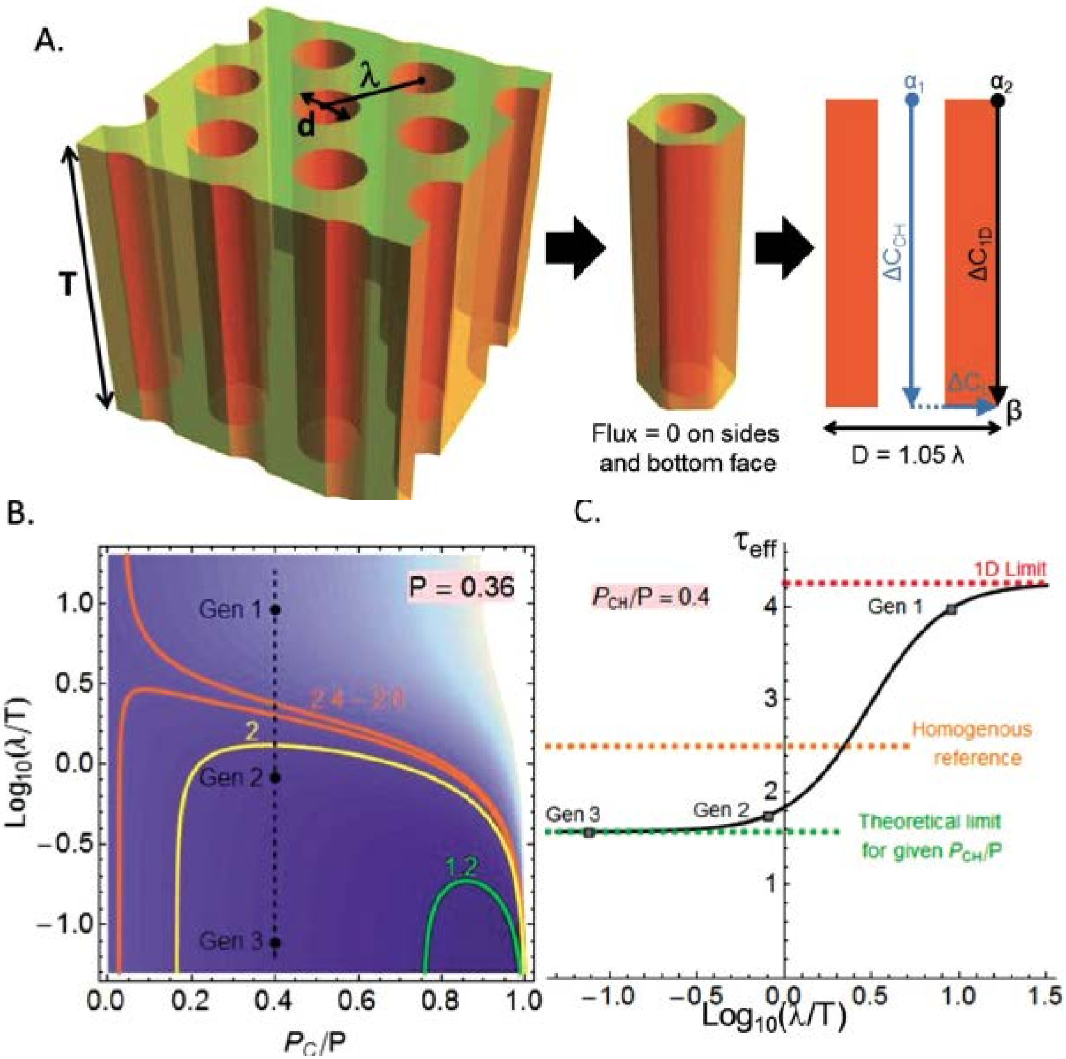
- Magnetic alignment produces aligned porosity *normal to the electrode plane* simply and quickly (in seconds).

- Both HPPC and DST tests show superior capacity to standard galvanostatic tests for thick, low-tortuosity electrodes. Sintered NCA electrodes reached 14 mAh/cm^2 area capacity in HPPC tests. DST tests at maximum pulse rates of 2C reached 8.1 mAh/cm^2 for mag-aligned and sintered $LiCoO_2$.

Technical Back up slides

Technical backup slide

Influence of channel spacing and channel pore fraction on tortuosity



d…channel diameter

λ... channel spacing

T… electrode thickness

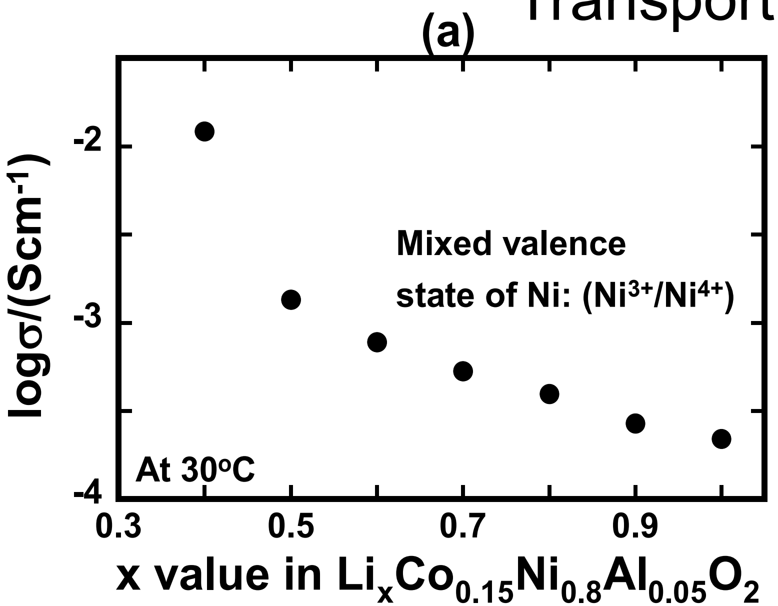
P_{CH}… pore fraction in channels

P… total pore fraction

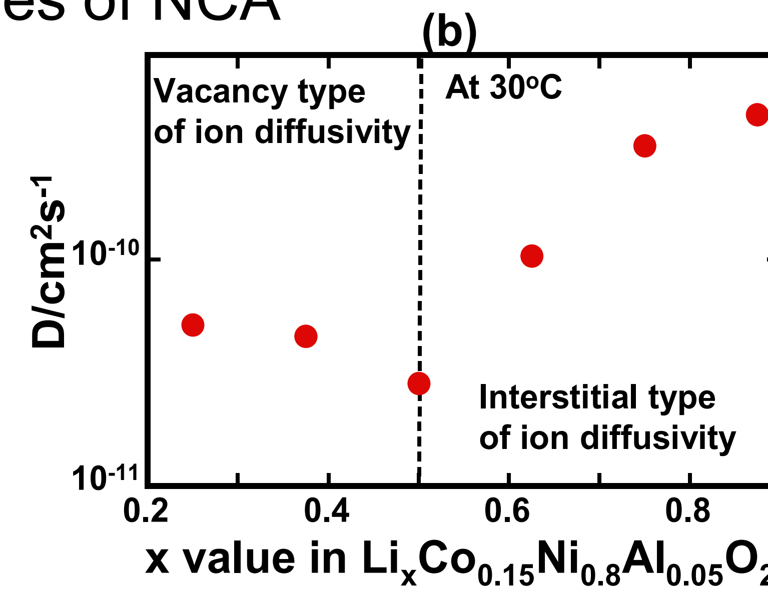
τ... tortuosity

Technical backup slide

Transport properties of NCA



Electronic conductivity of NCA vs. Li content



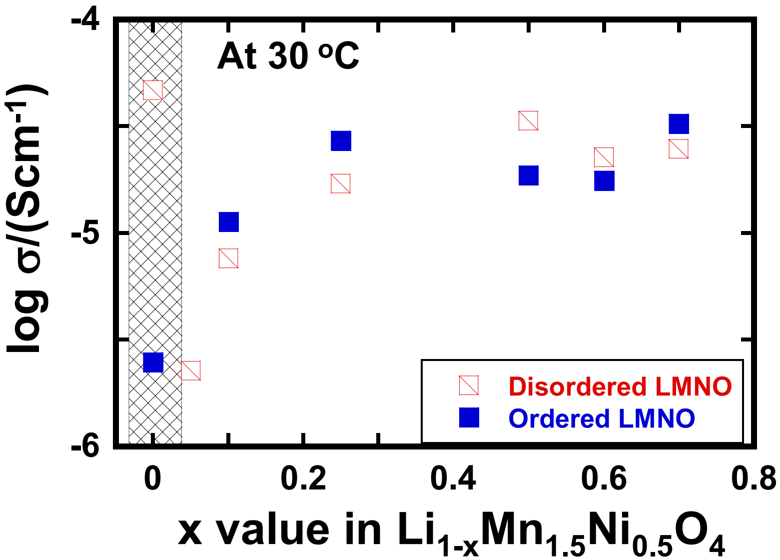
Ionic diffusivity of NCA vs. Li content

- (a) NCA has ~10^{-4}–10^{-3} S/cm electronic conductivity over the Li concentration range of interest. The electronic conductivity of NCA increases upon delithiation, but is always lower than that of $LiCoO_2$.
- (b) It appears that lithium diffusion mechanism changes from interstitial type to vacancy type around 50% delithiation state. Obtained data can be functioned with the lamellae thickness up to 8μm for higher cycling rate.

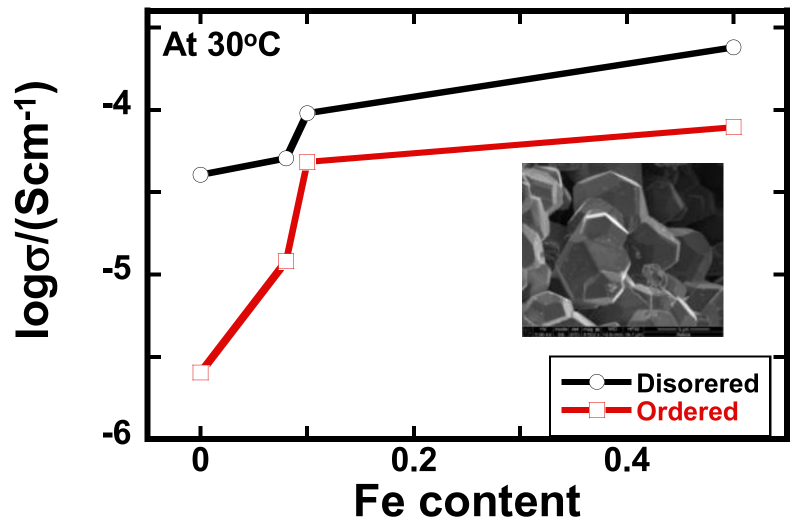
Technical backup slide

The transport properties of LMNO and Fe-LMNO:

Electronic conductivity vs. Li



Electronic conductivity vs. Fe doping



Samples (at 50°C)	Ionic conductivity (Scm^{-1})	Ionic diffusivity (cm^{2}s^{-1})	
$LiMn_{1.5}Ni_{0.5}O_4$	~2×10^{-7}	~10^{-7}	DC
$LiMn_{1.5}Ni_{0.5}O_4$	~6×10^{-8}	~5×10^{-8}	AC
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$	~8×10^{-8}	~6×10^{-8}	DC
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$	~6×10^{-8}	~9×10^{-8}	AC

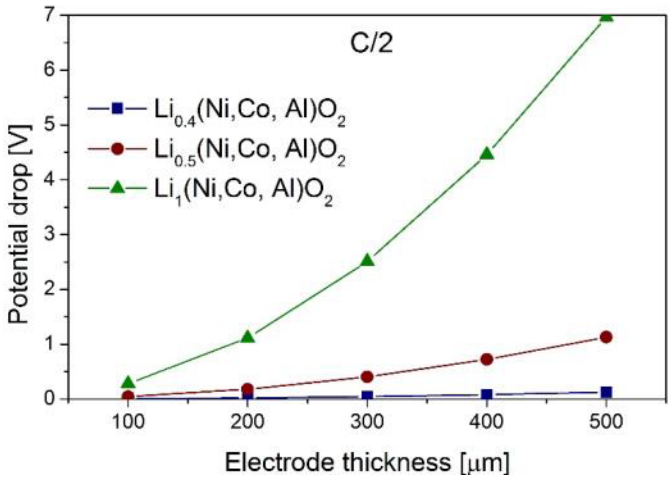
- Fe-LMNO selected for its resistance to electrochemical fracture
- Both LMNO and Fe-LMNO have a too low an electronic conductivity to use as a pure phase.
- Conductive additives would need to be incorporated for thick electrode applications.

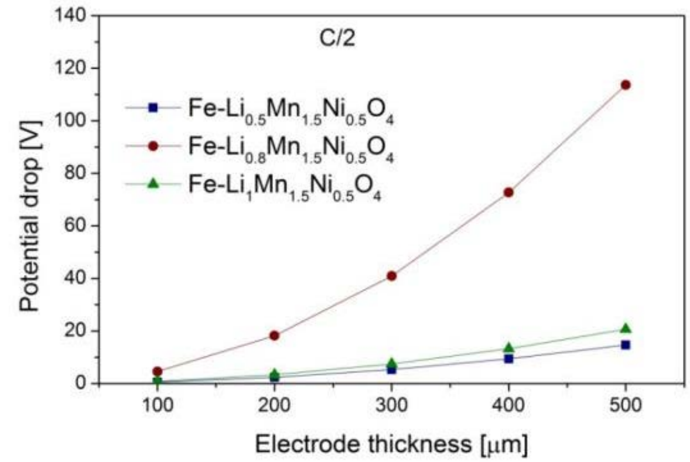
Technical backup slide

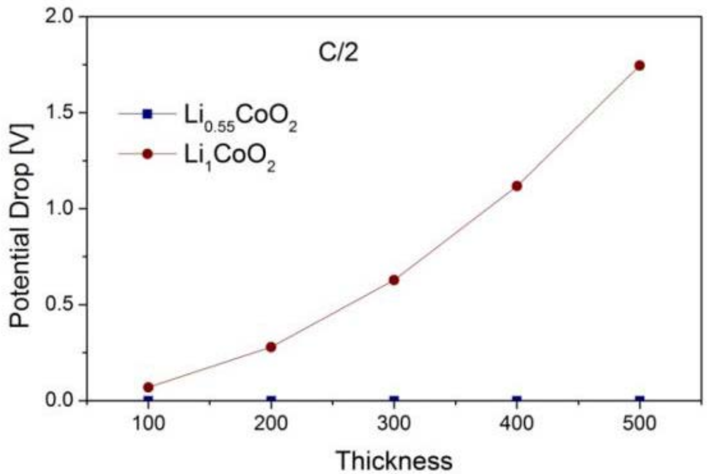
Estimation of Ohmic drop

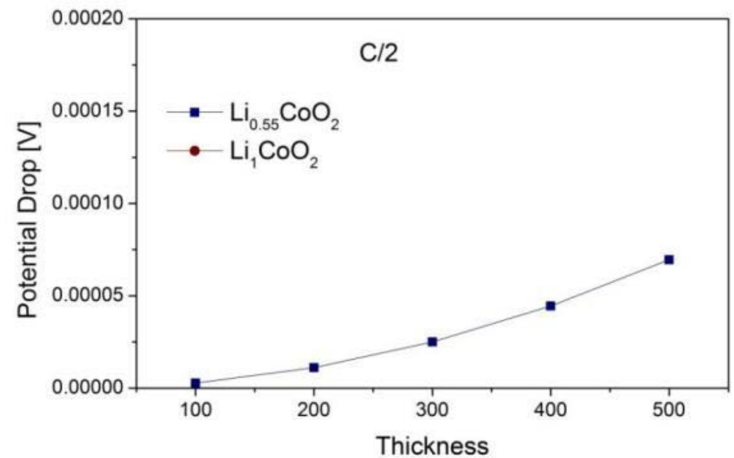
$$\Delta V = RI = t^2 \frac{1}{\sigma}\rho(1-p) * Crate * Cap$$

ΔV… voltage drop, R… resistivity, I… current [Ah], t…, thickness, ρ… density [g/cm³], A… area: 1cm², p… porosity, Crate [1/h], Cap… capacity [Ah/g], σ… conductivity,



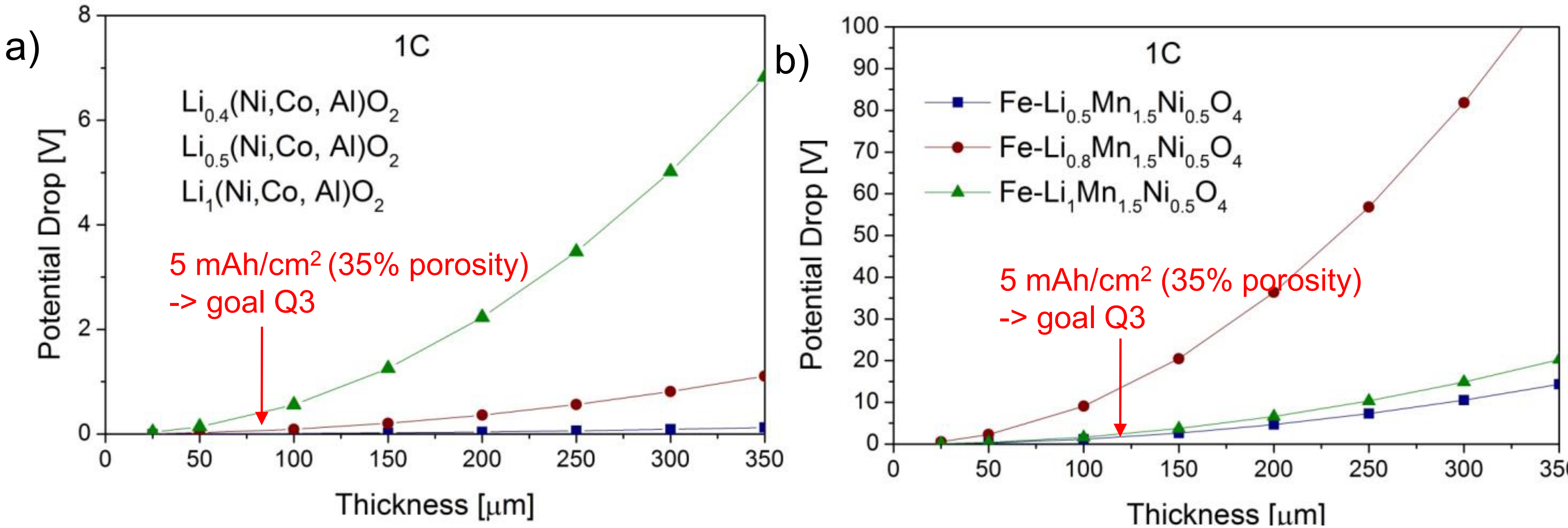






Technical Accomplishments

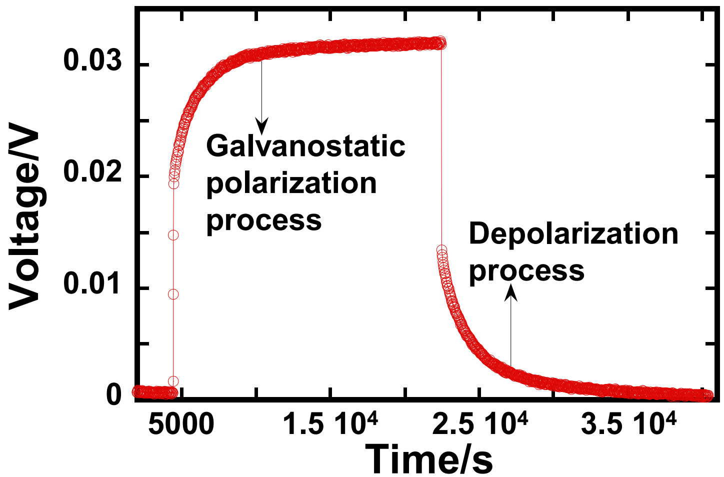
Potential drop vs. electrode thickness for fully dense NCA and Fe-LMNO



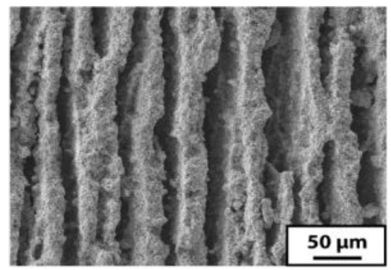
- Calculated for electronic conductivity at various Li contents. Note that cathodes in Li-ion cells are never fully lithiated after first cycle due to Li consumed in SEI formation
- Current density calculated on basis of measured capacities
- Potential drops are too large in Fe-doped LMNO to reach Q3 goal of 5 mAh/cm^2 at 1C rate – excluded from further consideration
- NCA to be evaluated further with electrochemical tests to establish true capacity vs. rate performance

DC polarization-depolarization measurement of effective diffusivity (and corresponding tortuosity)

5°C/min



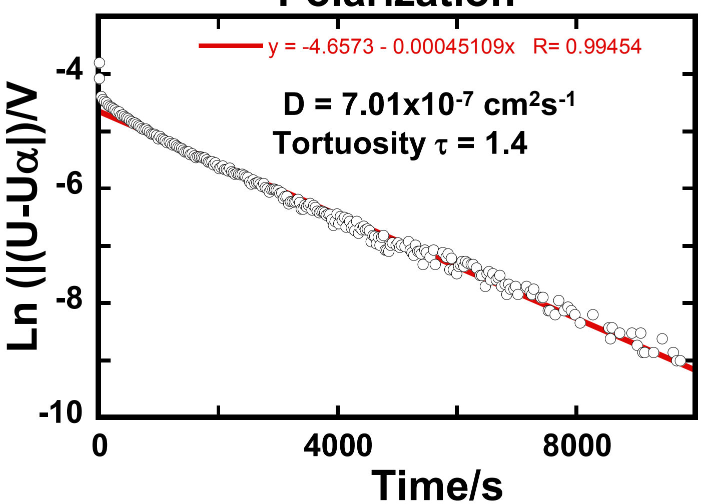
(a)-5°C/min



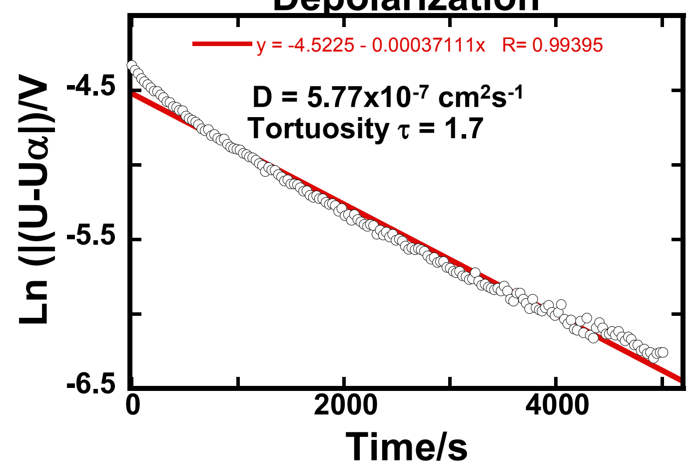
$$U_{ion} = \frac{i_p L}{\sigma_{tot}} + \frac{\sigma_{eon}}{\sigma_{tot}} \frac{i_p L}{\sigma_{ion}} \left\{ 1 - \frac{8}{\pi^2} \exp\left[-\frac{t}{\tau^{\delta}} \right] \right\}$$

$\ln(U - U_{\infty})$ vs. t

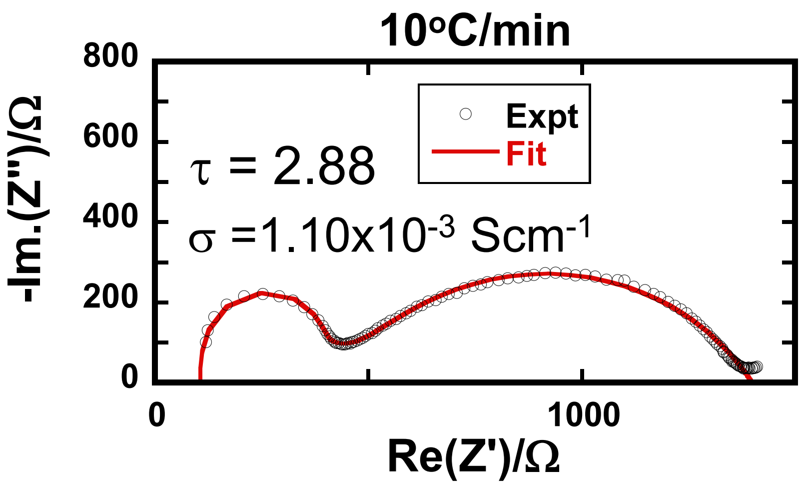
Polarization

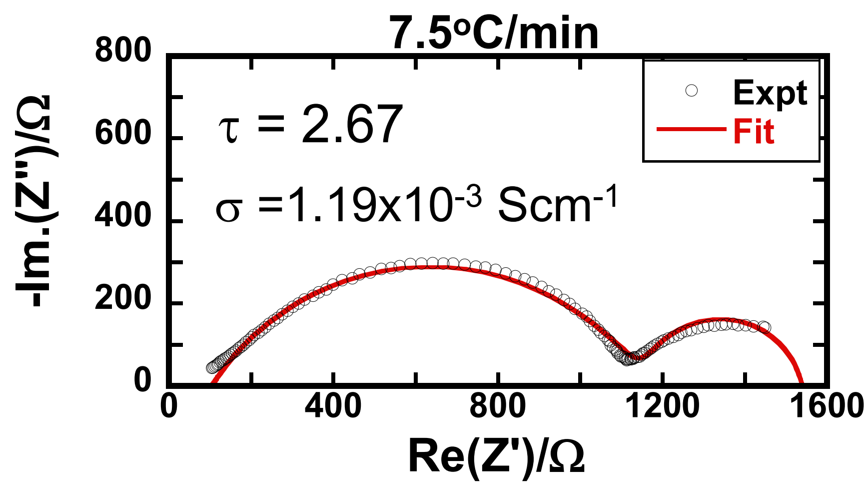


Depolarization



Impedance spectroscopy measurement of tortuosity is in good agreement with DC polarization/depolarization measurements

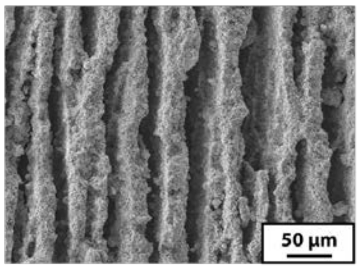


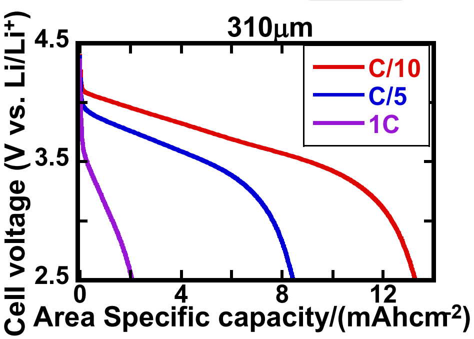


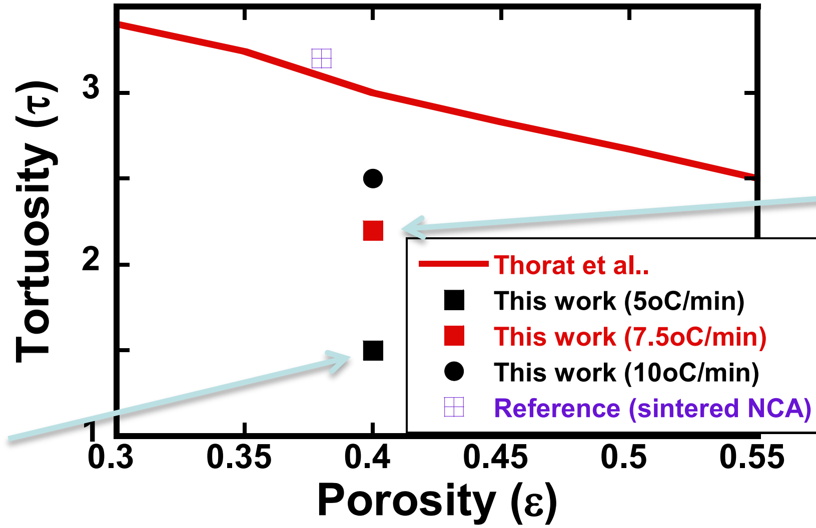
Samples	Tortuosity (τ)	Method
5°C/min	~1.5	dc
7.5°C/min	~2.2	dc
10°C/min	~2.5	dc
7.5°C/min	~2.6	ac
10°C/min	~2.8	ac

Tortuosity and rate performance

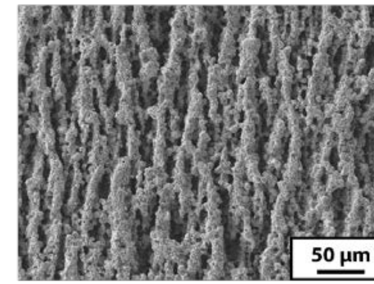
(a)-5°C/min

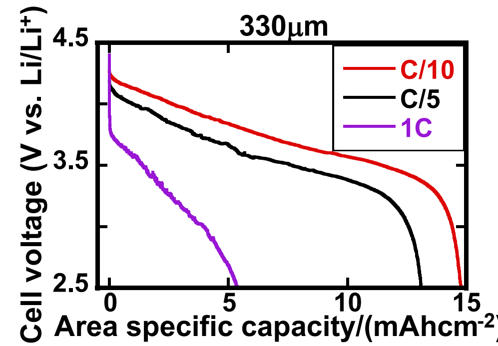






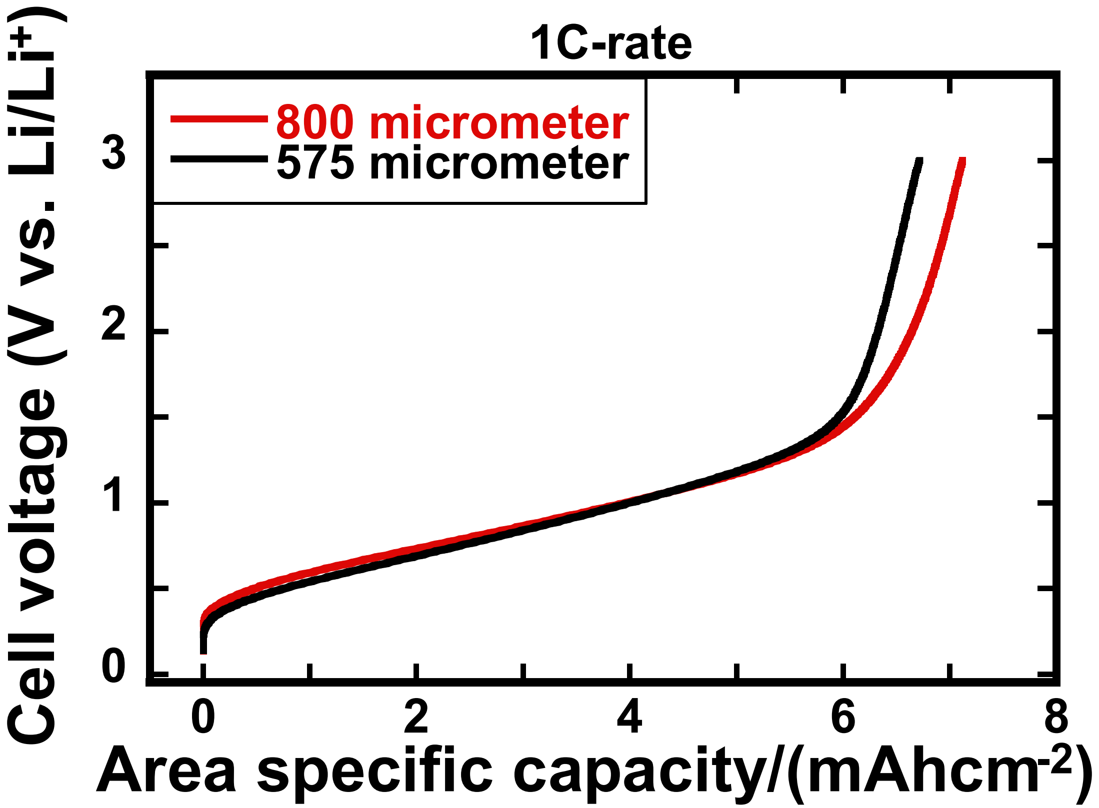
(b)-7.5°C/min





- 5 mAh/cm^2 at 1C rate met Q4 2014 milestone

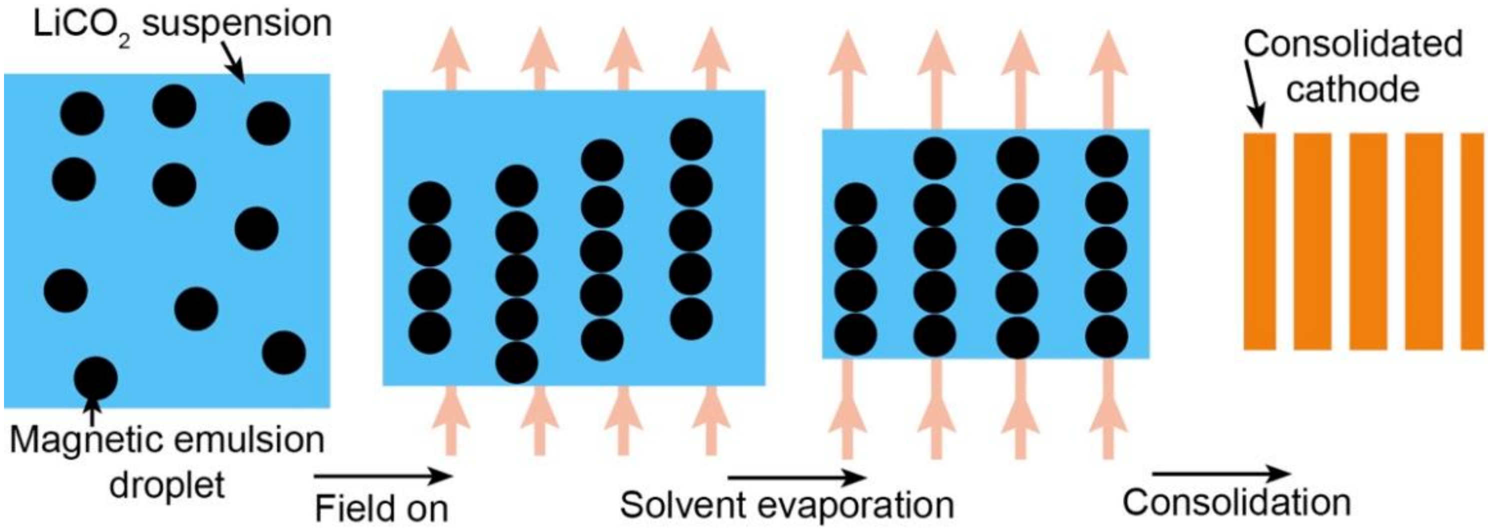
Q2 2015 Milestone: Demonstrate at least 5 mAh/cm² at 1C rate continuous cycling rate for at least one anode



575 µm = ~23 mA/cm²

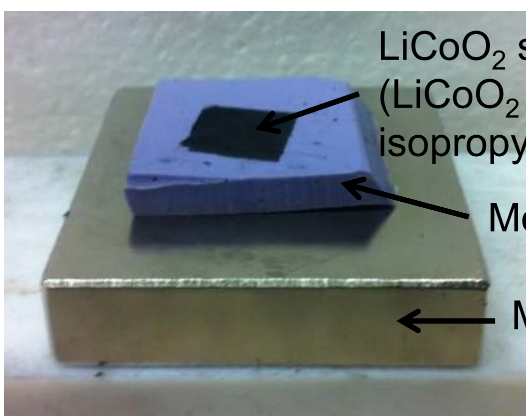
800 µm = ~21mA/cm²

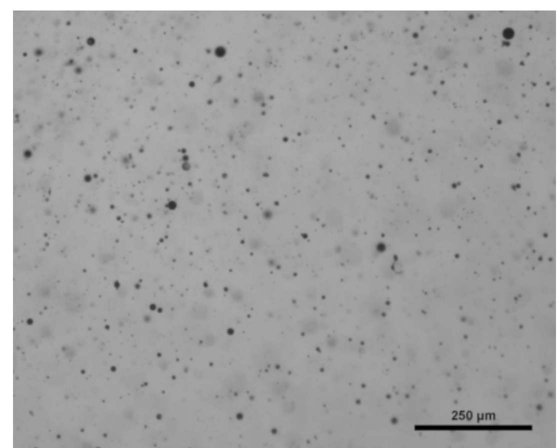
Fabrication of oriented porosity by magnetic chaining/alignment of emulsion droplets



Magnetic emulsion: 10 vol% Fe_3O_4 nanoparticles with surfactant in a hydrocarbon oil. Droplet size 1-10 µm

$LiCoO_2$ suspension: $LiCoO_2$ particles with binder and surfactant -> final Fe_3O_4 content <10 wt% of $LiCoO_2$





Play video